Restricted Rotation Involving the Tetrahedral Carbon. XXXI. Barriers to Rotation in 2,3-Dichloro-9-(1-cyano or 1-methoxycarbonyl-1-methylethyl)triptycenes[1)]

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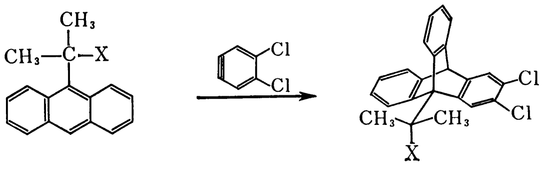
Synopsis. The title compounds were prepared to see the effects of substituents in 1-position on the barriers to rotation about the C_9–C_{subst} bond. The barrier was found to be higher for the cyano compound than those for the corresponding compounds carrying a substituent in 1-position, whereas the methoxycarbonyl compound gave almost the same barrier irrespective of the substituent.

In one of the preceding papers, we have shown that the barriers to rotation in 1-substituted 9-(1-cyano-1-methylethyl)triptycenes are always lower than that of 9,10-bis(1-cyano-1-methylethyl)triptycene[2)] and have suggested that 9-(1-cyano-1-methylethyl)triptycenes which do not carry a substiuent in 1-position should demonstrate a higher barrier to rotation due to the enhanced stability of the ground state of the rotamers.[3)] We wish to report in this paper that 2,3-dichloro-9-(1-cyano-1-methylethyl)triptycene (**1**), which lacks a substituent in 1-position, has shown a higher barrier than those with a substitutent in 1-position. Incidentally, the barrier to rotation of 2,3-dichloro-9-(1-methoxycarbonyl-1-methylethyl)-triptycene (**2**) is almost the same with those carrying a substituent in 1-position.

The syntheses of the compounds in question were carried out as was reported in the previous paper. Usually the ±*sc* form was obtained preferentially and the ±*sc* form (or a ±*sc*-form-rich mixture) was heated to obtain a ±*sc*-*ap* mixture. Chromatography of the ±*sc*-*ap* mixture gave the *ap* form.



1: X=CN
2: X=$COOCH_3$

Experimental

Spectral Measurement. ^1H NMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz. Infrared spectra were obtained with a Hitachi 260-30 infrared spectrometer.

Materials. Syntheses and isomerization were carried out as follows.

*2,3-Dichloro-9-(1-cyano-1-methylethyl)triptycene (**1**).* To a refluxing solution of 1.00 g (4.08 mmol) of 9-(1-cyano-1-methylethyl)anthracene and 1.0 ml of isopentyl nitrite in 35 ml of 1,2-dimethoxyethane, was slowly added 1.10 g (5.34 mmol) of 4,5-dichloroanthranilic acid[4)] in 15 ml of 1,2-dimethoxyethane under a nitrogen atmosphere. The mixture was heated for further 40 min and filtered. The solution was evaporated and the residue was chromatographed on alumina to give 727 mg of ±*sc*-**1**, mp 283—284 °C. Found: C, 73.65; H, 4.39; N, 3.56; Cl, 18.19%. Calcd for $C_{27}H_{17}Cl_2N$: C, 73.85; H, 4.39; N, 3.59; Cl, 18.17%. ^1H NMR ($CDCl_3$, δ): 2.43 (6H, s), 5.26 (1H, s), 7.0—7.2 (4H, m), 7.3—7.6 (3H, m), 7.45 (1H, s), 7.8—8.0 (1H, m), 7.95 (1H, s). IR (KBr): 2235 cm^{-1}.

Refluxing a solution of 337 mg of ±*sc*-**1** in 20 ml of *o*-dichlorobenzene overnight and subsequent chromatography on alumina gave 116 mg of *ap*-**1**, mp 233—235 °C. Found C, 73.56; H, 4.19; N, 3.76; Cl, 17.74%. Calcd for $C_{27}H_{17}Cl_2N$: C, 73.85; H, 4.39; N, 3.59; Cl, 18.17%. ^1H NMR ($CDCl_3$, δ): 2.43 (6H, s), 5.26 (1H, s), 7.0—7.2 (4H, m), 7.3—7.5 (2H, m), 7.54 (1H, s), 7.60 (1H, s), 7.8—8.1 (2H, m). IR (KBr): 2240 cm^{-1}.

*2,3-Dichloro-9-(1-methoxycarbonyl-1-methylethyl)triptycene (**2**)* was prepared similarly from 9-(1-methoxycarbonyl-1-methylethyl)anthracene and 4,5-dichlorobenzyne. The reaction gave a 6:1 ±*sc* and *ap* mixture in 38% yield after rough chromatography. ±*sc*-**2** was obtained in pure form by chromatography since this form was eluted first: mp 211—213 °C. Found: C, 71.11; H, 4.61; Cl, 16.48%. Calcd for $C_{25}H_{20}Cl_2O_2$: C, 70.93; H, 4.76; Cl, 16.75%. ^1H NMR ($CDCl_3$, δ): 2.27 (6H, s), 3.78 (3H, s), 5.20 (1H, s), 6.9—7.5 (7H, m), 7.39 (2H, s), 7.6—7.8 (1H, m). IR (KBr): 1735, 1715 cm^{-1}.

ap-**2**, mp 244—245 °C, was obtained similarly by isomerization of ±*sc*-**2** followed by chromatography. Found: C, 71.19; H, 4.70%. Calcd for $C_{25}H_{20}Cl_2O_2$: C, 70.93; H, 4.76%. ^1H NMR ($CDCl_3$, δ): 2.28 (6H, s), 3.77 (3H, s), 5.22 (1H, s), 6.9—7.1 (4H, m), 7.2—7.5 (4H, m), 7.47 (1H, s), 7.72 (1H, s). IR (KBr): 1740 cm^{-1}.

Kinetic Measurement. Solutions of compound **1** or **2** in 1-chloronaphthalene were heated by immersing the samples in appropriate boiling baths. The details were reported elsewhere.[3)]

Results and Discussion

Assignment of the ±*sc* structures was not straightforward, since both forms, ±*sc* and *ap*, gave a singlet signal for the methyl groups in ^1H NMR spectra. We took advantage of the method of syntheses and an aspect of ^1H NMR spectra for the structural assignments. Firstly, the formation of triptycenes from anthracenes and benzynes are known to be stereoselective to a large extent:[4)] the incoming benzynes prefer the antiperiplanar position of the largest group. It will be reasonable to assume that the ±*sc*-form is produced preferentially in this case as well as the similar cases reported elsewhere.[3)] Secondly, close examination of the NMR spectra in the aromatic region discloses that there are two singlets which are assignable to 1 and 4 protons. It may be reasonable to assume that the protons in 4-position give signals at almost the same chemical shift: a signal at δ 7.45 for the major product of **1** and that at δ 7.54 for the minor are due to 4-protons. Consideration of anisotropy effects of the cyano group[5)] leads to the conclusion

TABLE 1. RATES OF ISOMERIZATION, EQUILIBRIUM CONSTANTS AND THERMODYNAMIC PARAMETERS FOR THE PROCESSES $\pm sc \rightleftharpoons ap$ OF COMPOUNDS **1** AND **2**

X	T / °C	k ($\pm sc \rightarrow ap$) / s^{-1}	k ($ap \rightarrow \pm sc$) / s^{-1}	K ($\pm sc/ap$)	ΔH / kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}
CN	189	5.99×10^{-5}	1.34×10^{-4}	2.24	−7.5	−22.6
	179	1.88×10^{-5}	3.81×10^{-5}	2.02		
	162	4.47×10^{-6}	9.11×10^{-6}	2.04		
	152	1.14×10^{-6}	2.07×10^{-6}	1.82		
$COOCH_3$	189	3.57×10^{-4}	1.00×10^{-3}	2.80	−1.3	−11.3
	179	1.88×10^{-4}	5.22×10^{-4}	2.78		
	162	3.54×10^{-5}	8.92×10^{-5}	2.52		
	152	1.44×10^{-5}	4.06×10^{-5}	2.82		

TABLE 2. KINETIC PARAMETERS FOR THE INTERNAL ROTATION OF COMPOUNDS **1** AND **2**

X	Process	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	E_a / kJ mol^{-1}	log A
CN	$\pm sc \rightarrow ap$	164.8	27.2	168.6	14.8
	$ap \rightarrow \pm sc$	172.4	49.8	176.0	16.0
$COOCH_3$	$\pm sc \rightarrow ap$	141.4	−7.5	145.0	13.0
	$ap \rightarrow \pm sc$	142.7	3.8	146.4	13.6

that the 1-proton in ±*sc*-**1** should give a signal at a lower field than *ap*-**1**. This supports the conclusion that the major product is ±*sc*-**1**. Similarly, of the two signals due to 1-protons of ±*sc*-**2** and *ap*-**2**, the signal due to 1-proton of ±*sc*-**2** should be at a higher field than that of *ap*-**2**. The signals at δ 7.39 for the major product is an overlap of those due to 1- and 4-protons and is at a higher field than the signal at δ 7.72 for the minor product. Thus the major product is again the ±*sc* form of **2**.

The equilibrium constants and the rates of isomerization obtained at various temperatures are listed in Table 1. From these values thermodynamic parameters were obtained as also shown in Table 1. Kinetic parameters were obtained by both Eyring plot and Arrhenius plot and are shown in Table 2.

Since the Arrhenius activation energy for rotation of 9-(1-cyano-1-methylethyl)triptycenes which carry a chloro or a methyl group in 1-position is about 150 kJ mol^{-1},[3] those of compound **1** are at least 12 kJ mol^{-1} higher than the former. Thus the barrier to rotation, being the difference in energies between the transition state and the ground state, is high for compound **1** because of the stability of the ground state, although the energy of the transition state for rotation is expected to be lower than that for the corresponding compounds carrying a peri-substituent.

It is interesting to note that the free energy of activation for rotation in compound **2** at 177 °C (143.1 kJ mol^{-1}) is about the same with the corresponding compounds carrying a substituent in 1-position, although in the latter two processes, ±*sc*→*ap* and *ap*→±*sc*, a fairly large difference has been seen because of the instability of the *ap* form. This phenomenon may to attributed to the raise of the ground state relative to the cyano compound (**1**) because the methoxycarbonyl group is a large group in a plane which causes severe interaction with the triptycyl moiety.

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